

## INFLUENCE OF DRYING METHODS ON DENSITY AND POROSITY OF MILK POWDER GRANULES

### SUMMARY

Gas and liquid displacement techniques were used to determine the true and apparent densities as well as the relative porosities of milk powder granules produced by various drying techniques. Using helium as the displacing gas, rapid penetration of conventional spray-dried, spray-dried foam and vacuum-dried foam particles was noted; all whole milk powders had true densities averaging  $1.30 \text{ g/cm}^3$ . By this method, the measured true density of a commercial instantized skimmilk powder was  $1.48 \text{ g/cm}^3$ . When hydrogen, nitrogen, decalin, or mercury was used as a displacing medium, data were obtained showing a wide variation in the porosity of particles produced by different drying techniques. It was concluded that conventional spray-dried material contained small amounts of occluded gas exchanged only with great difficulty, if at all. Spray-dried foam particles contain relatively large volumes of gas which can undergo exchange slowly and completely. The small quantities of trapped gas in vacuum foam-dried particles can undergo rapid and complete exchange.

During the course of a study of the effect of the physical structure of various types of milk powder on their dispersibility and keeping quality, variations in rate of gas penetration into various types of milk powders were noted which could be related to their relative porosity.

We are here reporting the observed effect of various milk-drying techniques on the relative porosity of milk powder particles and the true and apparent densities of these particles as measured by gas and liquid displacement.

When measuring the densities of the solids in the powder granules, we found considerable difference in the flow rates of helium, hydrogen, and nitrogen into, and out of, these powders. The flow rates were similar to those observed by Barrer et al. (3) through various zeolites known as molecular sieves. These materials have micropores of molecular dimensions through which gas flow is greatly impeded. Flow through such pores does not follow the Poiseuille or Knudsen formulation, but rather involves surface flow in an adsorbed layer of gas, involving a considerable energy of activation (11). A similar situation apparently exists in some types of milk powder granules.

Factors influencing gas movement in conventional spray-dried powders have previously been studied by Coulter and Jenness (6). A number of workers have determined the density

of this type of powder using mineral oil (10), hexane (5), and gas displacement (9).

### MATERIALS AND METHODS

Three samples of whole milk powder dried by different methods in the Dairy Products Laboratory pilot plant, and one commercial instantized skimmilk powder sample purchased off the supermarket shelf in Washington, D. C., were used. The whole milk powders were conventional spray-dried powder, a high vacuum shelf foam-dried powder according to the method of Sinnamon et al. (16) and a foam-spray dried powder according to the method of Hanrahan et al. (7).

All the gases used were purchased from the Southern Oxygen Company.<sup>1</sup> The He was purified by passing through a charcoal trap maintained at  $-195^\circ \text{C}$ , previously degassed at  $250^\circ \text{C}$ . Electrolytic  $\text{H}_2$  was purified with a Deoxo<sup>1</sup> catalytic  $\text{H}_2$  purifier, followed by a charcoal trap at  $-195^\circ \text{C}$ . Prepurified  $\text{N}_2$  was used after passing through a liquid  $\text{N}_2$  trap to remove any trace of moisture.

The decalin was purchased from the Fisher Scientific Company<sup>1</sup> and was used without further purification.

<sup>1</sup> The use of trade names is for the purpose of identification only, and does not imply endorsement of the product or its manufacturer by the U. S. Department of Agriculture.

Mercury densities were measured by Prado Laboratories,<sup>1</sup> Cleveland, Ohio, using an Aminco-Winslow<sup>1</sup> Porosimeter and calculated from the Hg penetration at pressures of 20 lb/sq in.

Decalin densities were measured according to the method of Manus and Ashworth (10). The solubility effect of the decalin on the constituents of the milk powder was checked by comparing decalin filtered from completed density determinations with unused stock decalin in a Brice-Phoenix<sup>1</sup> differential refractometer. No change in index of refraction was observed. Microscopic examination showed that the integrity of the powders was maintained when suspended in decalin.

In the gas displacement method an all-glass gas adsorption apparatus as commonly used for surface area measurements (1) was used for the volume determinations. It consists of a calibrated gas burette and a mercury manometer equipped with a fine adjustment control (1) to adjust the mercury level and an electronic contact indicator (1, 13) located at the zero reference point. The gas burette is jacketed and kept at a constant temperature of 26.2°C with a Labline<sup>1</sup> model no. 3052 high-precision ( $\pm 0.02^\circ\text{C}$ ), constant-temperature circulating system. The sample tube is immersed in another bath maintained at the same temperature as the burette. The apparatus is evacuated with a mercury diffusion pump backed by a mechanical oil pump. Pressures as low as  $0.005 \mu$ , as measured with a McLeod gauge, have been consistently obtained.

The density measurements were carried out in the following manner: A clean, dry sample tube is attached to the apparatus and evacuated to  $0.005 \mu$ . A quantity of He is admitted from a reservoir into the burette and the pressure is recorded. The stopcocks in the line leading into the sample tube are then opened and the pressure read again after equilibrium. At constant temperature the volume of the tube is readily obtained, using Boyle's law. The sample tube is then removed and filled with a weighed amount of powder and the volume is again measured in the same manner. The difference between the volume of gas required to fill the sample tube when empty and when containing the powder is the sample volume.

The density so determined with He is the true chemical density, as the He fills all the voids between the particles as well as any pore space due to cracks, crevices, etc., internal to the particle. Only completely sealed-off cavities within the particles will remain undetected. Mercury densities, however, are only apparent

densities, as a nonwetting liquid such as Hg will not enter any pores at the pressure used.

Powder porosities were then calculated from the equation

$$\frac{1}{\rho_a} - \frac{1}{\rho_t} = V_p \quad (1)$$

where  $V_p$  is the pore gram per gram and  $\rho_a$  and  $\rho_t$  are the apparent and true densities, respectively. The porosity defined as the percentage of particle volume which is pore space is then given by  $\theta = V_p \rho_a$ . (2)

#### RESULTS

When nitrogen was used as the displacing gas, the pressure in the system did not remain constant, but showed a slow decrease with time with all the spray-dried powders used. This means that there is a slow increase in the volume of gas required to fill the pore space in the sample and accordingly there is a slow creep or increase in the density of the material with time.

In Figure 1 we have plotted the density in g/cm<sup>3</sup> of conventional spray-dried whole milk powder against time in hours. As shown, a constant density value is reached very quickly with He, but with N<sub>2</sub> there is a slow creep, with the density never reaching the He value. The behavior with H<sub>2</sub> is somewhat anomalous. The change in density with time is more rapid than for N<sub>2</sub> but slower than with He, but eventually it does reach the He value and finally exceeds it.

The molecular diameters of the gases used are 2.00 Å for He, 4.00 Å for N<sub>2</sub>, and 2.18 Å for H<sub>2</sub> (15). The presence of micropores of molecular dimensions would explain the differences observed in the behavior with the gases. Nitrogen being much larger than the others cannot pass through these pores as

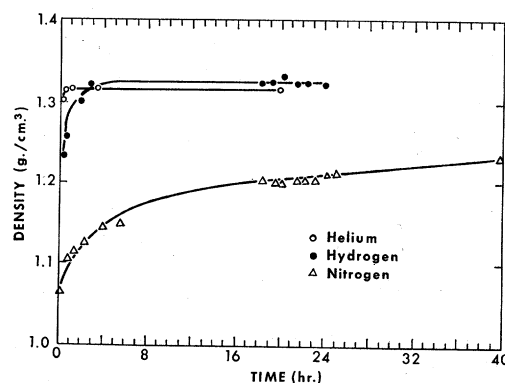


FIG. 1. Variation in density of conventional spray-dried powder with time using He, H<sub>2</sub>, and N<sub>2</sub> as displacing gases.

readily; hence, the slower rate of penetration. There are some pores completely inaccessible to the  $N_2$  molecule; hence, the lower ultimate density value with  $N_2$ . The intermediate penetration rate obtained with  $H_2$  is in accord with its molecular diameter, being between He and  $N_2$ . The high ultimate value finally obtained with  $H_2$  is probably due to some other cause, such as a chemical reaction.

Figure 2 shows a somewhat similar pattern for foam-spray powder.

By plotting the nitrogen densities against time for three different whole milk powders (Figure 3) one has a measure of the relative porosities of these powders. The vacuum-shelf foam-dried powder has essentially no micropore structure, as the He and  $N_2$  densities were identical and both were reached rapidly. The

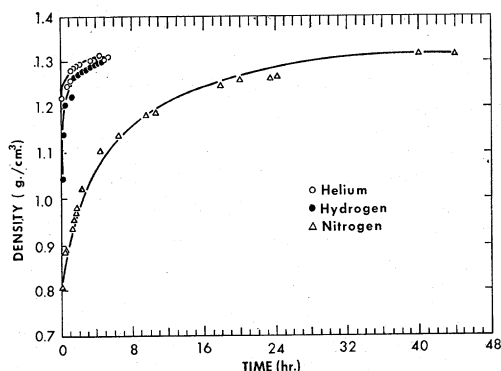


FIG. 2. Variation in density of foam-spray powder with time using  $N_2$ ,  $H_2$ , and He as displacing gases.

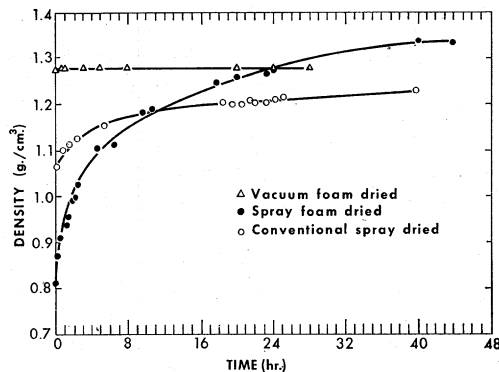


FIG. 3. Variation in nitrogen-density of several whole milk powders with time.

foam-spray powder apparently has a large network of micropores small enough to slow down the flow of  $N_2$ , but large enough to permit the  $N_2$  density to finally reach the He value. The conventional spray-dried powder is much less porous than the foam spray, but the pores existing there have much smaller radii; hence, the very slow, long creep in density with time. In this case the pore sizes are such that the  $N_2$  density never reached the He value.

Relative porosities may readily be seen from the density values listed in Table 1.

Using equation (1), total pore volumes, and the volume  $Q_t$ , the pore space filled with  $N_2$  as a function of time was obtained. This is, then, the volume of gas occluded or sorbed by the powder. We use the vague term sorbed rather than absorbed or adsorbed, as it is probably a combination of several things—trapping or

TABLE 1  
Densities of dried milk powders in  $g/cm^3$

Displacing medium	He	$N_2$	$H_2$	Hg	Decalin
Powder					
Foam spray	1.311	0.738 <sup>a</sup> 0.809 <sup>b</sup> 1.316 <sup>c</sup>	1.040 <sup>d</sup> 1.300 <sup>e</sup>	0.451	0.798
Conventional spray	1.308	1.069 <sup>f</sup> 1.237 <sup>g</sup> 1.243 <sup>h</sup>	1.231 <sup>i</sup> 1.326 <sup>j</sup>	0.835	1.056
Vacuum foam	1.278	1.278	.....	1.126	1.278
Commercial instant skim	1.483	1.339	.....	1.203	1.337

<sup>a</sup> Initial value at  $P = 146.3$  mm Hg.

<sup>b</sup> Initial value at  $P = 798.1$  mm Hg.

<sup>c</sup> Value at  $P = 738.9$  mm Hg after 44 hr.

<sup>d</sup> Initial value at  $P = 806.6$  mm Hg.

<sup>e</sup> Value at  $P = 776.1$  mm Hg after 5 hr.

<sup>f</sup> Value at  $P = 758.9$  mm Hg after 13 min.

<sup>g</sup> Value at  $P = 733.3$  mm Hg after 50.4 hr.

<sup>h</sup> Value at  $P = 509.8$  mm Hg after 173.3 hr.

<sup>i</sup> Value at 864.4 mm Hg after 21 min.

<sup>j</sup> Value at 847.8 mm Hg after 24 hr.

occlusion within the particles, capillary condensation, solid solution formation, and possibly some surface adsorption.

#### DISCUSSION

The rate of sorption in the spray-dried powders showed a pressure dependence (Figure 4).

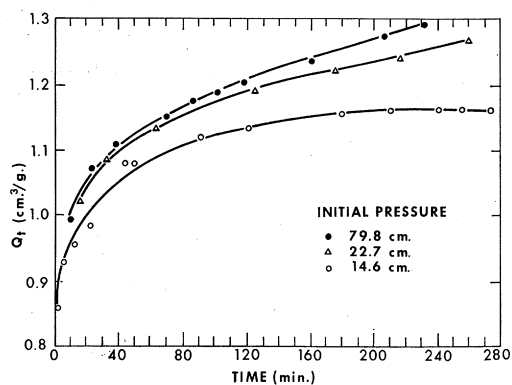


FIG. 4. Effect of initial pressure of  $N_2$  upon sorption rate in foam-spray-dried powder.

With higher initial pressures the penetration rate increases; however, it is not proportional to the pressure; as the pressure is increased further there is a relatively smaller increase in the diffusion rate. Conversely, the relative rate,  $Q_t/Q_\infty$ , expressed as the per cent of total sorption occurring in a given time interval, decreases as the pressure of the gas increases.

This behavior is in complete agreement with diffusion theory (2, 4). For a thin slab with a pressure equilibrium existing on both sides we have the equation:

$$Q_t = Lc \left[ 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left( \frac{-D(2m+1)^2 \pi^2 t^2}{L^2} \right) \right] \quad (3)$$

for the amount  $Q_t$  diffusing in time  $t$  where  $L$  is the path length for the diffusion and  $c$  is the concentration. For the quantity  $Q_t$  at time unity we have:

$$Q_t = Lc \left[ 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left( \frac{-D(2m+1)^2 \pi^2}{L^2} \right) \right] \quad (4)$$

A plot of the volume sorbed against equilibrium pressure yielded isotherms of the type shown in Figure 5. An equation of the form

$$\frac{C}{(C_s - C)P} = K \quad (5)$$

can be applied to these isotherms where  $C$  is the concentration and  $C_s$  is the saturation concentration. Substituting into Equation (4) gives:

$$Q_{t=1} = LK'KC_s \frac{P}{1 + KP} \quad (6)$$

and if  $P$  is large enough we have the approximation:

$$Q_{t=1} = LK'C_s \quad (7)$$

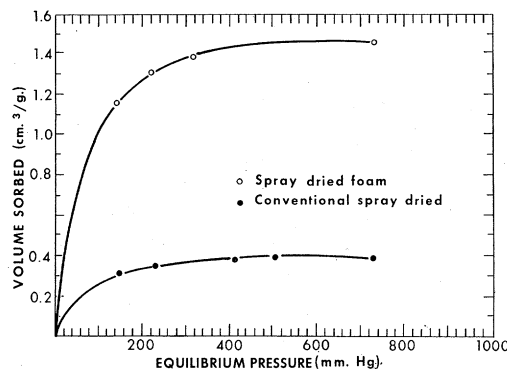


FIG. 5. Sorption isotherms for  $N_2$  in spray-dried powders at 26 C.

Hence, the theory predicts that in a system such as is present in the spray-dried milk powders there is a point beyond which further increases in pressure will not be effective to increase the diffusion rate.

Mervyn Jones (11, 12) has treated the problem of flow through pores of molecular dimensions in terms of an equation involving three types of flow: Poiseuille, Knudsen, and surface flow in an adsorbed layer. He uses the equation:

$$Q = \frac{\pi n \bar{r}^4 \bar{M} \bar{P} (P_1 - P_2)}{8 l \eta R T} + \frac{\lambda \bar{n} r^3 4 (2 \pi M / R T)^{1/2} (P_1 - P_2)}{3 \bar{l}} + \frac{2 \pi n \bar{r}^2 \bar{v} (m_1 - m_2)}{\bar{l}} \quad (8)$$

where  $\bar{r}$  = average pore radius

$\bar{l}$  = average pore length

$\lambda$  = mean free path of diffusing species

$\bar{P}$  = mean pressure

$\eta$  = gas viscosity

$(P_1 - P_2)$  = pressure difference along  $\bar{l}$

$\bar{v}$  = a term for the molecular diameter of the diffusing species

$(m_1 - m_2)$  = the difference in concentration of adsorbed material along the pore length  $\bar{l}$

and all the other terms have their usual significance.

When the pore diameter is of the order of the diameter of the  $N_2$  molecule  $\bar{v} \approx 2 \times 10^{-8}$  cm. Substituting this value into Mervyn Jones's equation the first two terms, corresponding to Poiseuille and Knudsen flow, respectively, are negligible and surface flow will predominate.

Flow of this type should require a considerable energy of activation for the molecules of the diffusing species to squeeze through such narrow capillaries. Comparison of our results with calculated values based on low-temperature measurements (8) bear this out.

Considering Mervyn Jones's equation we see that only Poiseuille and Knudsen flow are pressure-dependent, whereas surface flow depends only on the concentration of the adsorbed species. Greater pressure differentials should, then, have little effect upon the rate of diffusion through the dried milk powders, particularly in the linear portion of the isotherm (Figure 5), as has been shown (Figure 4).

From the data obtained in this study, we have concluded that a relatively large percentage of the gas moving into or out of milk powder particles does so by surface diffusion along pore walls. Since the rate of this process depends only on the concentration gradient along the pore length, it may be assumed that oxygen located within the interior of milk powder particles can be removed by flushing the powder bed with pure nitrogen. Under these conditions the rate of removal of absorbed oxygen may be higher than that obtained by holding the particles under high vacuum (14). A comparative study of rates of oxygen removal from milk powders by nitrogen flushing and vacuum degassing is now in progress in our laboratory.

#### REFERENCES

- (1) BARR, W. E., AND ANHORN, V. J. *Scientific and Industrial Glass Blowing and Laboratory Techniques*. pp. 257-283. Instruments Publ. Co., Pittsburgh. 1959.
- (2) BARRER, R. M. *Diffusion in and Through Solids*. Cambridge University Press, Cambridge. 1941.
- (3) BARRER, R. M., AND IBBITSON, D. A. Occlusion of Hydrocarbons by Chabazite and Analcite. *Trans. Faraday Soc.*, 40: 195. 1944.
- (4) BARRER, R. M., AND IBBITSON, D. A. Kinetics of Formation of Zeolitic Solid Solutions. *Trans. Faraday Soc.*, 40: 206. 1944.
- (5) BECKETT, D. C., EMMONS, D. B., AND ELLIOTT, J. A. The Determination of Bulk Density, Particle Density and Particle Size Distribution in Skim Milk Powder. XVth Intern. Dairy Congr., Sec. V.1: 913. 1962.
- (6) COULTER, S. T., AND JENNESS, R. Packing Dry Whole Milk in Inert Gas. *Minnesota Agr. Expt. Sta., Tech. Bull.* 167. 1945.
- (7) HANRAHAN, F. P., TAMSMA, A., FOX, K. K., AND PALLANSCH, M. J. Production and Properties of Spray-Dried Whole Milk Foam. *J. Dairy Sci.*, 45: 27. 1962.
- (8) HOWARD, N., FOX, K. K., HOLSINGER, V. H., AND PALLANSCH, M. J. The Specific Surface Areas of Milk Powders Produced by Various Drying Methods. *J. Dairy Sci.*, 44: 1155. 1961.
- (9) LEA, C. H., MORAN, T., AND SMITH, J. A. B. The Gas Packing and Storage of Milk Powder. *J. Dairy Research*, 13: 162. 1943.
- (10) MANUS, L. J., AND ASHWORTH, U. S. The Keeping Quality, Solubility and Density of Powdered Whole Milk in Relation to Some Variations in the Manufacturing Process. II. Stability and Density. *J. Dairy Sci.*, 21: 935. 1948.
- (11) MERVYN JONES, W. Mobility in a Sorbed Layer. I. The Flow of Gases and Vapors Through Porous Media. *Trans. Faraday Soc.*, 47: 381. 1951.
- (12) MERVYN JONES, W. Mobility in a Sorbed Layer. II. Surface Flow Through Pores of Molecular Dimensions. *Trans. Faraday Soc.*, 48: 562. 1952.
- (13) MILLS, B. A Sensitive Contact Indicator. *Rev. Sci. Instr.*, 12: 105. 1941.
- (14) MILTON, R. M., AND JONES, R. A. Desorption of Oxygen-Contaminated Molecular Sieves. U. S. Pat. No. 3,023,841. March 6, 1962.
- (15) MOORE, W. J. *Physical Chemistry*. p. 179. Prentice Hall, Englewood Cliffs, N. J. 1955.
- (16) SINNAMON, H. J., ACETO, N. C., ESKEW, R. K., AND SCHOPPET, E. F. Dry Whole Milk. I. A New Physical Form. *J. Dairy Sci.*, 40: 1036. 1957.